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(54) Accelerated steel strip pickling process and device for carrying out the process

(57) A process for the continuous pickling in a non-oxidizing acid bath of hot-rolled steel strips, characterised in that the strip is subject to the pickling action of the bath, additioned of a pickling catalyst, under turbulent conditions. An embodiment of the device apt to carry out the aforesaid process is shown in figure 1.

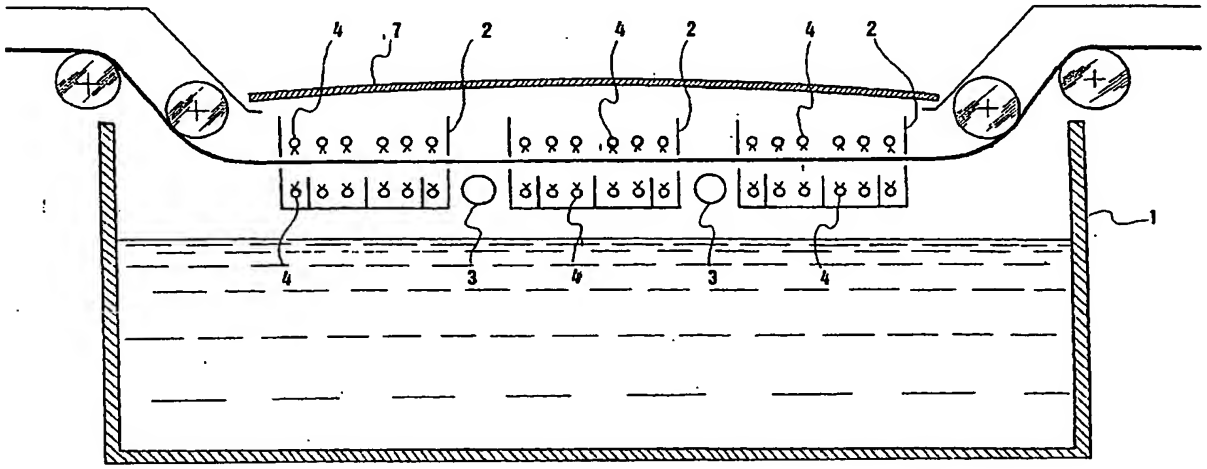

FIG.1

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Description

[0001] The present invention relates to the continuous pickling in a non-oxidizing acid bath of hot-rolled strips of magnetic and stainless ferritic steels.

[0002] As it is known, often annealed and non-annealed magnetic steels and some annealed stainless steels have surface oxides, as scale and/or internal oxidation, highly adherent and with low reaction rates inside the conventional non-oxidizing pickling baths. Oxides possibly remaining on the surface after the pickling can cause serious inconveniences in the downstream treatments, and can interfere with the magnetic characteristics and the surface finishes of the two types of steel considered.

[0003] At present, the state of the art substantially provides three possible interventions for obtaining pickled surfaces that are completely clean of oxides. The first intervention comprises the use of non-oxidizing pickling baths with very lengthy immersion times. The second possible intervention comprises the addition of hydrofluoric acid to the pickling bath. Lastly, the third type of intervention comprises the use of oxidizing baths with the entailed cost-effectiveness and environmental impact drawbacks. However, none of those extremely aggressive methods can preserve the non-oxidized matrix of the underlying steel. Moreover, the adoption of the first type of intervention (anyhow including lengthy treatment times that entail negative repercussions on productivity) is hindered by the occurrence of inconveniences due to operational problems, whereas the adoption of the second and of the third type of intervention are hindered by cost-effectiveness and environmental protection reasons.

[0004] Therefore, notwithstanding research efforts, in the specific field object still remains for a pickling process that is simple, fast, cost-effective and of a negligible environmental impact.

[0005] The present invention permits to satisfy this object, further showing other advantages that will be apparent hereinafter.

[0006] Following the above, the present invention is related to a process for the continuous pickling, in a non-oxidizing acid bath, of hot-rolled steel strips, characterised in that the strip to be pickled is subject to the pickling action of the bath additioned with a pickling catalyst, under turbulent conditions.

[0007] In the most general case thereof, the pickling catalyst is at least one organic compound including at least one thiolic group. Satisfactory results were obtained with an organic compound comprising at least one thiolic group selected from a list comprising thioglycolic acid, its ammonium chloride, and combinations thereof.

[0008] The concentration of the organic compound comprising a thiolic group inside the pickling bath is comprised in the range 0.005-0.01 moles/litre.

[0009] A further object of the present invention is a device apt to carry out the aforedescribed process.

[0010] This device is characterised in that it comprises the following components in combination:

- a closed storage tank containing the catalyst-additioned pickling bath;
- at least one cell, located above the free surface of the pickling bath, inside which the strip to be pickled, possibly guided by supporting rolls, travels horizontally;
- immersed nozzles, provided above and below the strip, located and shaped so as to feed under pressure the pickling bath to the cell, to create a directional flow of the pickling bath itself that generates the required turbulent conditions;
- means for drawing the pickling bath from the tank and delivering it to the nozzles; and
- means for recirculating the pickling bath from the cell to the tank.

[0011] The means for drawing the pickling bath from the tank and delivering it to the nozzles can be a pumping circuit.

[0012] The means for recirculating the pickling bath from the cell to the tank can be a slit-shaped overflow inside the cell from which the bath cascades into the tank.

[0013] The cell body can be monolithic and integral with the storage tank, or it can be made of two overlapped portions, the lower thereof being integral with the tank, whereas the upper thereof is integral with the cover of the tank, thus being movable.

[0014] The most important technical effect yielded by the invention is that of accelerating the mass transfer at the interface with the surface to be pickled, and in performing a mechanic action to ease the detachment of oxide residues therefrom.

[0015] The present invention can be applied to the conventional pickling baths inclusive of non-oxidizing acids, thereby increasing the pickling capacity thereof.

[0016] The invention can also be applied with reasonable costs to the extant immersion pickling lines in order to improve/accelerate the performances thereof.

[0017] The accelerating effect is most evident for oriented and nonoriented, hot-rolled, annealed or non annealed magnetic steels, and the annealed ferritic stainless steels (AISI 400).

[0018] The deriving combined effect permits to obtain for the magnetic steels, the quantity of dissolved material being equal, clean surfaces with 30 to 60% shortened immersion times, even in presence of internally oxidized zones that usually are not easily pickled. Alternatively, the final performance being equal, the temperature and/or the acidity of the pickling bath can be decreased. The yielded surfaces are clean of oxides, and smoother than the ones yielded by the non-additioned pickling systems.

[0019] Likewise results are obtained with the ferritic

stainless steels (series 400) for which the pickling rate can be doubled.

[0020] So far, only a general description of the present invention has been provided. A more detailed description of some specific embodiments thereof will hereinafter be provided with reference to the figures and examples, aimed at making better understood the objects, characteristics, advantages and operational modes thereof.

[0021] Figure 1 is a schematic side view of an embodiment of the turbulence tank according to the present invention.

[0022] Figure 2 is a schematic front view of the embodiment of the turbulence tank according to the invention depicted in figure 1.

[0023] Figure 3 shows the weight loss values function of the pickling time, and the linear interpolation for a non-oriented magnetic steel (Si= 3%, Al= 0.5%), pickled in a pickling solution including hydrochloric acid at 80°C, with and without the application of the present invention.

[0024] Figure 4 shows the weight loss values function of the pickling time, and the linear interpolation for an AISI 430 stainless steel, pickled in a pickling solution including sulphuric acid at 80°C, with and without the application of the present invention.

Example 1

[0025] A 2-mm thick nonoriented magnetic steel (Si= 3.0%, Al= 0.5%) in a hot-rolled annealed state was immersed for increasing times in a pickling solution including 140 g/l HCl, 90 g/l FeCl2, at 80°C, under static conditions. Then the test was repeated using a turbulence cell according to the present invention, in presence of 0.006 moles/l accelerating additive.

[0026] With reference to figures 1 and 2, the closed storage tank containing the catalyst-additioned pickling bath is indicated with 1, the three cells in a sequence, having the top portion thereof integral to the movable cover 7 of the tank are indicated with 2, positioned above the free surface of the bath, inside which the strip to be pickled, guided by supporting rolls 4, travels horizontally. The reference number 5 indicates submersed nozzles, located above and below the strip, positioned and shaped so as to feed under pressure the pickling bath to the cell, thereby creating a directional flow of the pickling solution itself that generates the required turbulent conditions.

[0027] The reference number 6 indicates the pumping circuit that draws the solution from the storage tank and delivers it to the nozzle batteries.

[0028] The pickling solution exits by the overflow from each cell through the slit 7 and cascades into the tank 1.

[0029] The concentration of the accelerating additive (thioglycolic acid) in the pickling solution is 0.005 moles/l.

[0030] The results reported in figure 3 show that, weight losses being equal, the application of the present invention permits a 30 to 60% reduction in the immersion time, or that, immersion times being equal, an approximate 30% increase of the weight loss is obtained.

Example 2

[0031] An AISI 430 stainless steel, hot-rolled and annealed, was immersed for increasing times in a pickling solution including 200 g/l H2SO4, 80 g/l FeSO4, at 80°C, under static conditions. Then the test was repeated using the turbulence device according to the present invention adopted in example 1, in presence of 0.005 moles/l accelerating additive.

[0032] The results reported in figure 4 show that, weight losses being equal, the application of the present invention permits a 65% reduction in the immersion time, or that, immersion times being equal, a 165 to 220% increase in weight loss is obtained.

Claims

1. A process for the continuous pickling, in a non-oxidizing acid bath, of hot-rolled steel strips, characterised in that the strip to be pickled is subject to the action of the pickling bath, additioned with a pickling catalyst, under turbulent conditions.

2. The process for the continuous pickling, in a non-oxidizing acid bath, hot-rolled steel strips according to claim 1, wherein the pickling catalyst is at least one organic compound comprising at least one thiolic group.

3. The process for the continuous pickling of hot-rolled steel strips in a non-oxidizing acid bath according to claim 2, wherein the organic compound comprising at least one thiolic group is selected from a list comprising thioglycolic acid, its ammonium chloride and combinations thereof.

4. The process for the continuous pickling of hot-rolled steel strips in a non-oxidizing acid bath according to any one of the preceding claims, wherein the catalyst concentration inside the pickling bath is comprised in the range 0.005-0.01 moles/litre.

5. A device apt to carry out the process according to claims 1 to 4, characterised in that it comprises the following components in combination:

   - a closed storage tank (1) containing the catalyst-additioned pickling bath;
   - at least one cell (2), positioned above the surface of the pickling bath, inside which the strip to be pickled, possibly guided by supporting rolls (3), travels horizontally.
   - immersed nozzles (4), located above and be-

low the strip, positioned and shaped so as to feed under pressure the pickling bath to the cell (2), in order to create a directional flow of the pickling bath itself that generates the required turbulent conditions;

- means (5) for drawing the pickling bath from the tank (1) and delivering it to the nozzles (4); and
- means (6) for recirculating the pickling bath from the cell (2) to the tank (1).

6. The device according to claim 5, wherein the means (5) for drawing the pickling bath from the tank (1) and delivering it to the nozzle (4) is a pumping circuit.

7. The device according to any one of the claims 5 and 6, wherein the means (6) for recirculating the pickling bath from the cell (2) to the tank (1) is a slit-shaped overflow, inside the cell, wherefrom the pickling bath cascades into the tank (1).

8. The device according to any one of the preceding claims, wherein the body of the cell is monolithic and integral with the storage tank (1).

9. The device according to any one of the claims 5 to 7, wherein the body of the cell is made of two overlapped portions, the lower thereof is integral with the tank (1), whereas the upper thereof is integral with the cover (7) of the tank, and therefore is movable.

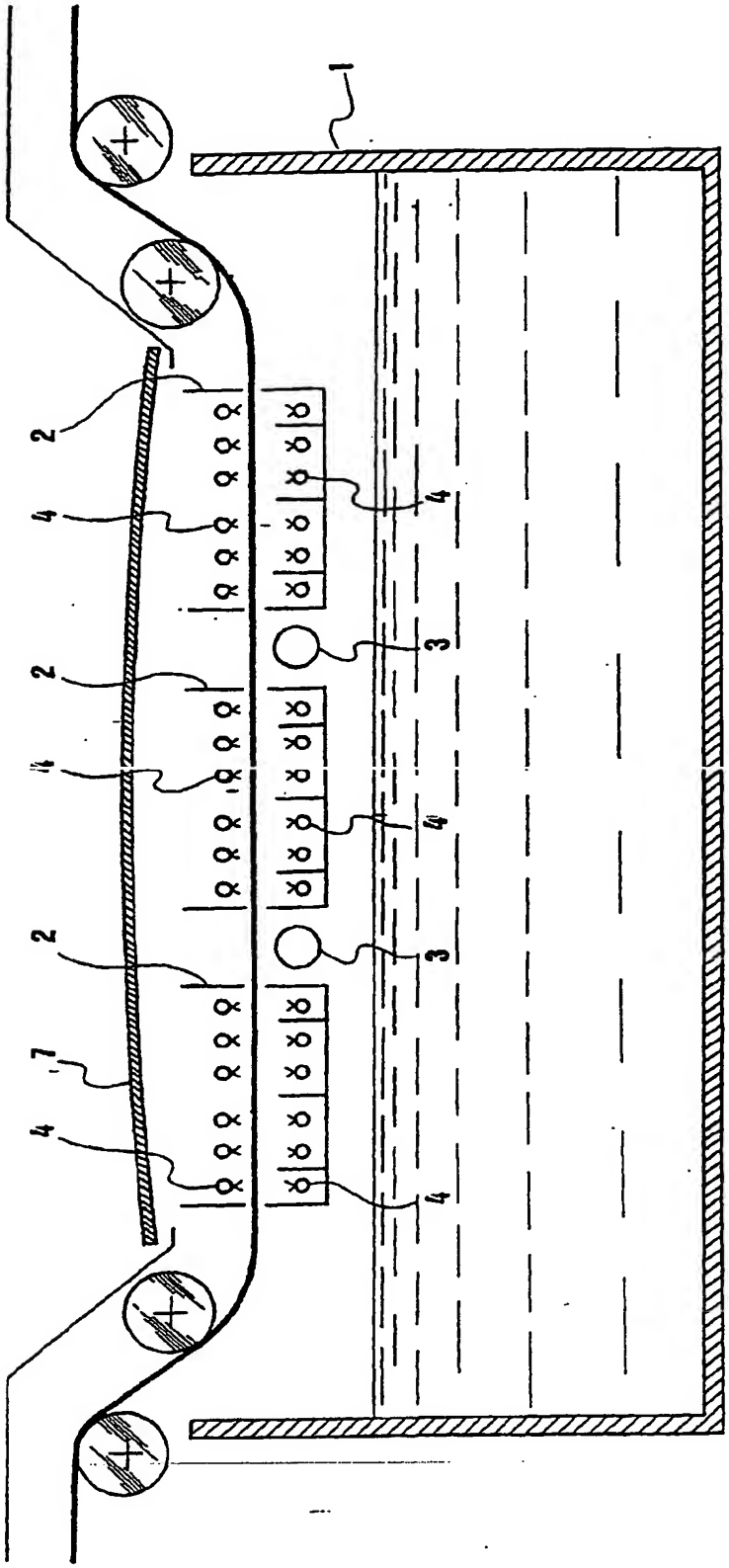

FIG.1

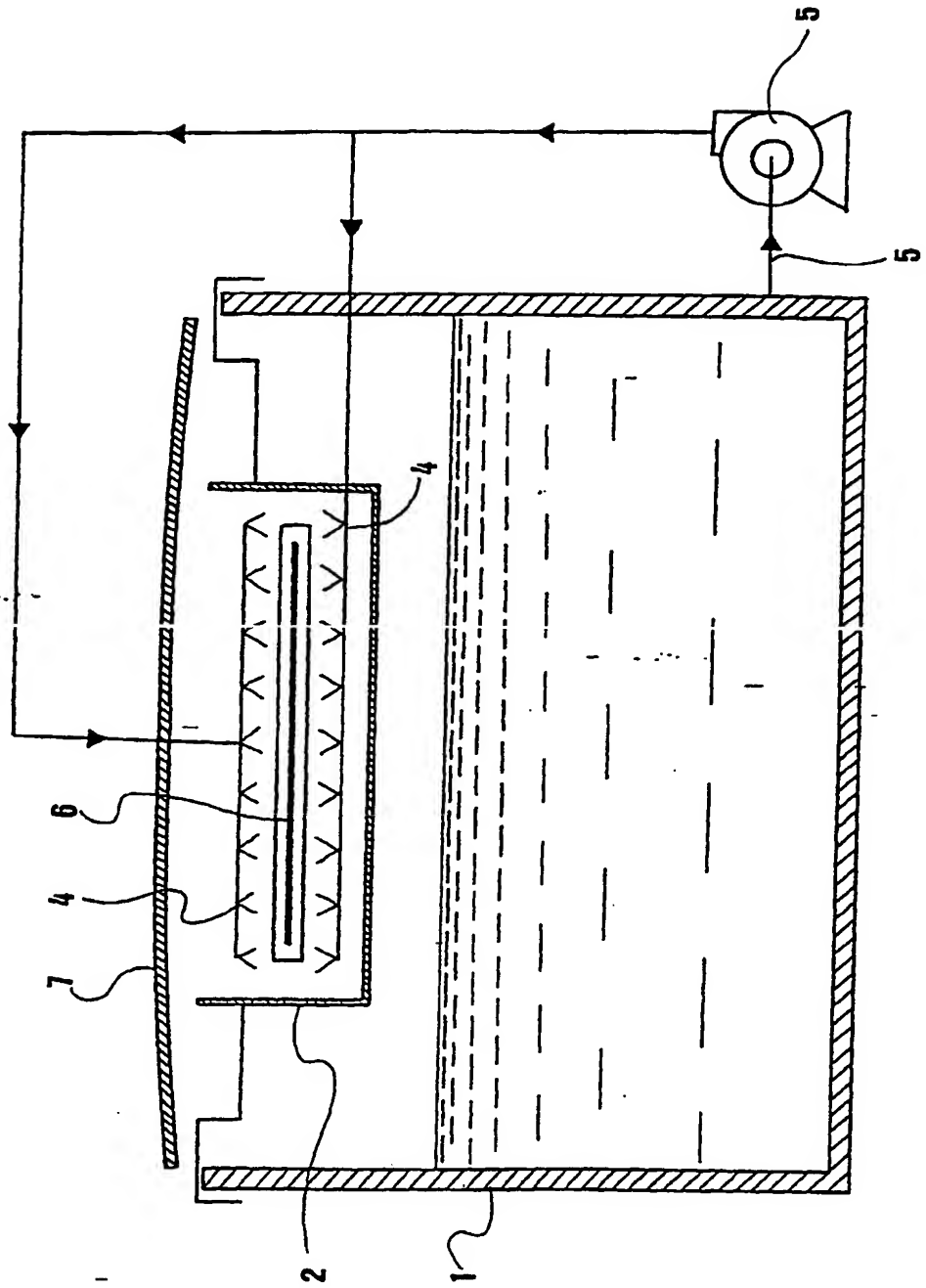

FIG.2

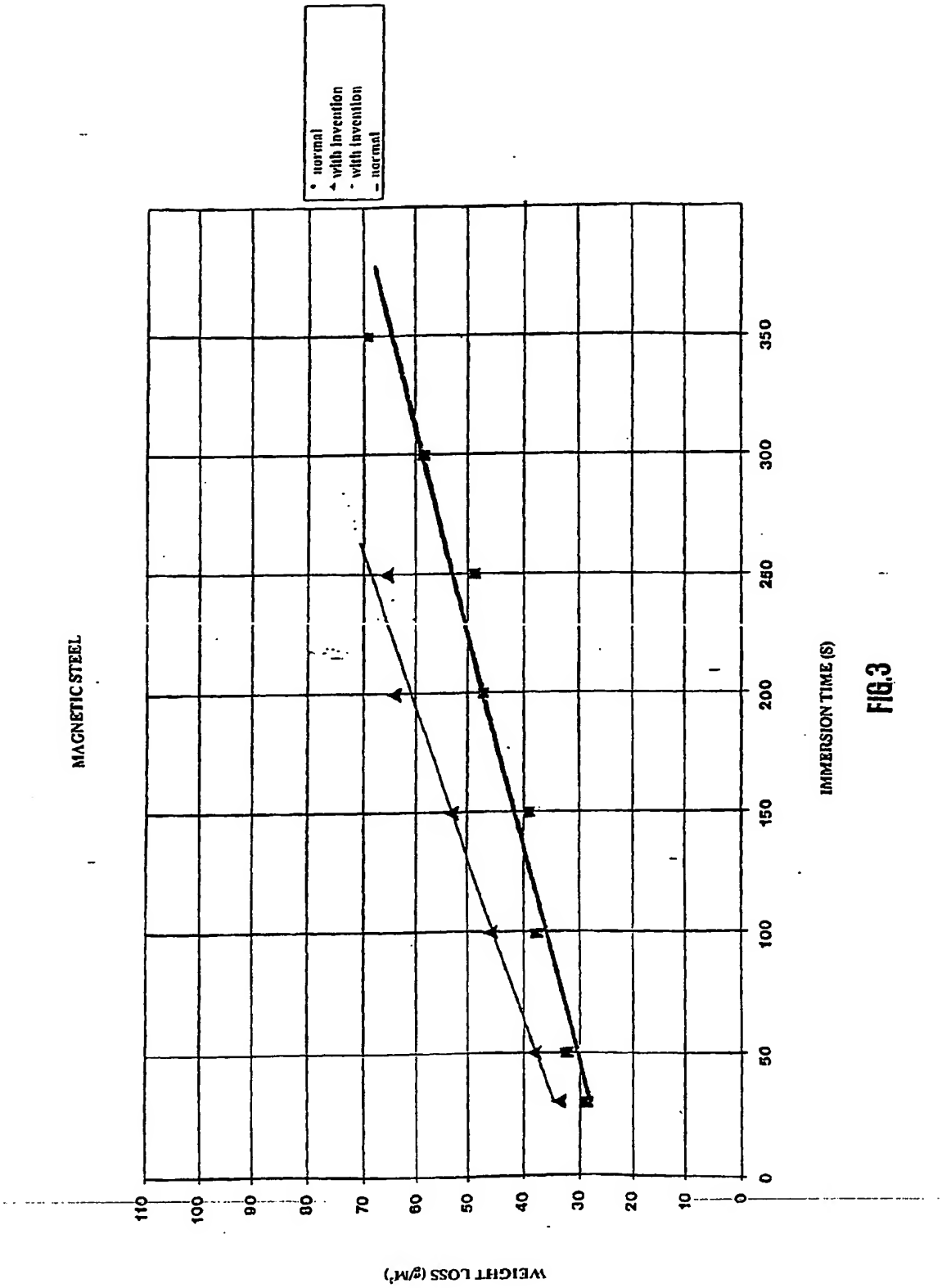
• normal
▲ with invention
- with invention
_ normal
MAGNETIC STEEL
IMMERSION TIME (S)
WEIGHT LOSS (g/M²)
0
50
100
150
200
250
300
350
10
20
30
40
50
60
70
80
90
100
110

FIG.3

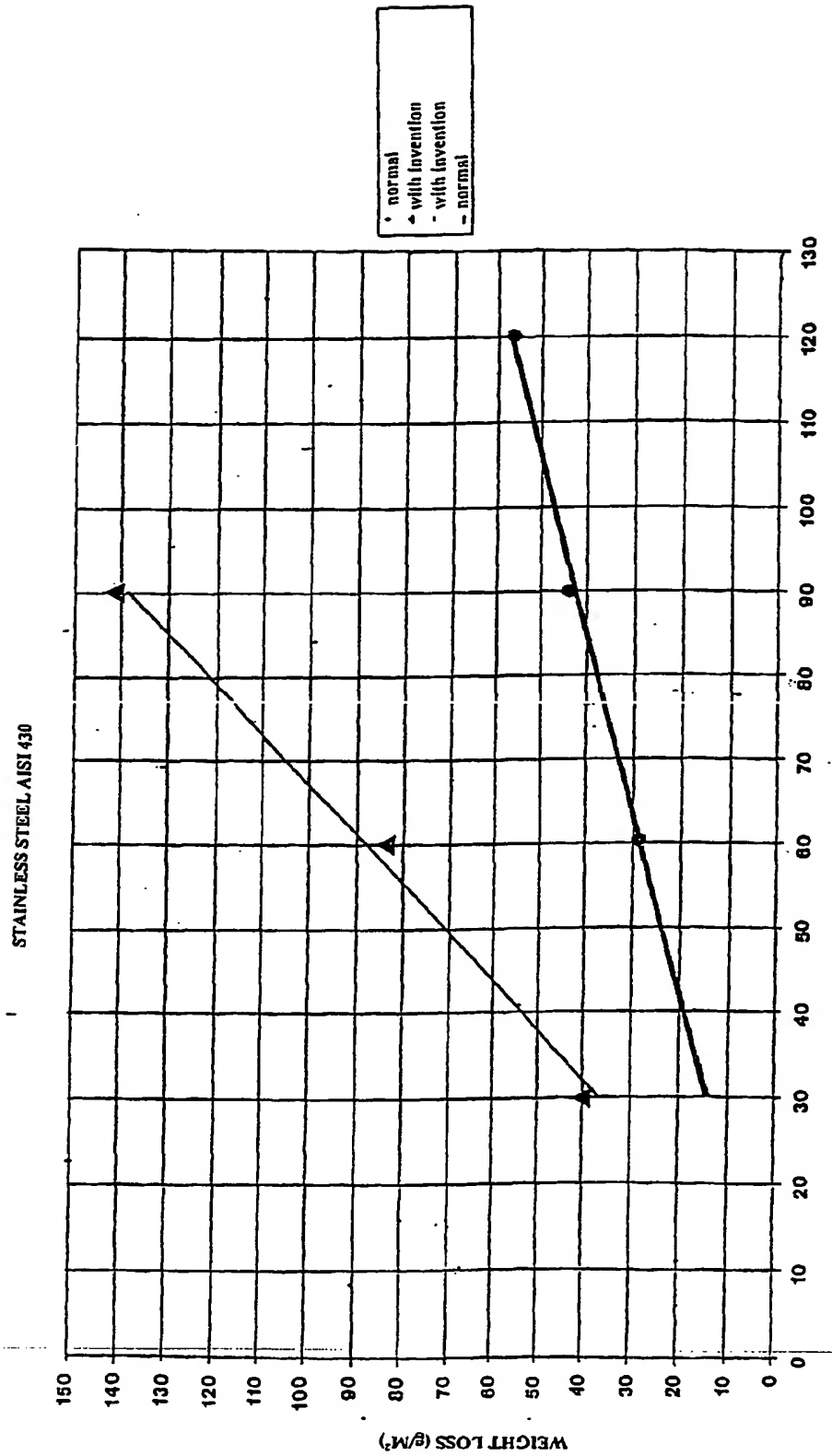
• normal
◆ with invention
- with invention
– normal
STAINLESS STEEL AISI 430
WEIGHT LOSS (g/M²)
IMMERSION TIME (S)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

FIG.4

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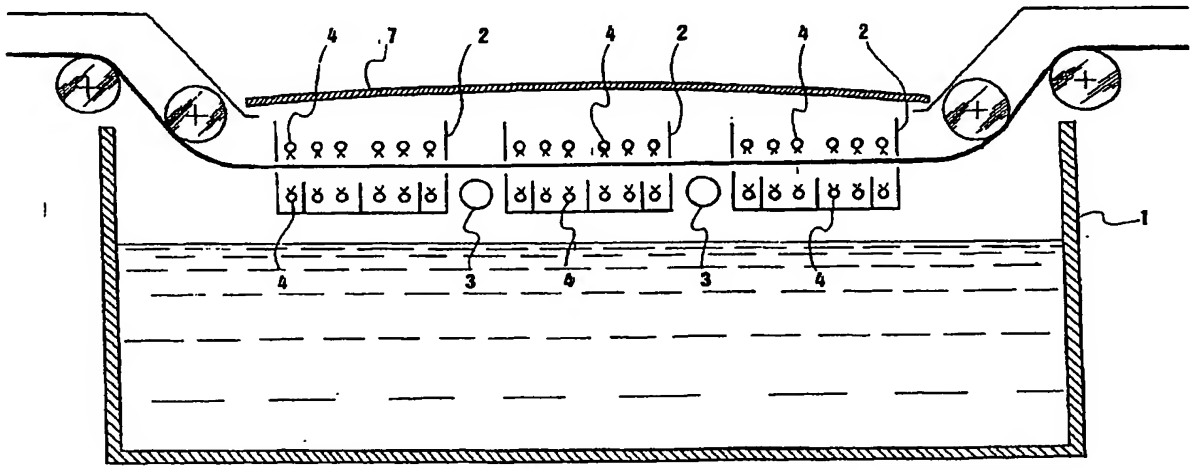

FIG.1

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EUROPEAN SEARCH REPORT

Application Number
EP 99 83 0766

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 September 2000	Torfs, F

CATEGORY OF CITED DOCUMENTS

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Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

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